

M.L. 2016, Chp. 186, Sec. 2, Subd. 04I Project Abstract

For the Period Ending September 30, 2018

PROJECT TITLE: Membrane-Based Process for Decentralized Drinking Water Production

PROJECT MANAGER: Santiago Romero-Vargas Castrillón

AFFILIATION: UMN, Dept. Civil, Environmental, and Geo- Engineering

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FUNDING SOURCE: Environment and Natural Resources Trust Fund

LEGAL CITATION: M.L. 2016, Chp. 186, Sec. 2, Subd. 04I

APPROPRIATION AMOUNT: \$190,000

AMOUNT SPENT: \$70,540.53

AMOUNT REMAINING: \$120,459.47

Overall Project Outcome and Results

The main outcome of this project is a novel surface modification protocol for water treatment membranes. We showed that graphene oxide coatings, known to exhibit antibacterial properties, improve the efficiency with which the membranes remove micropollutants, such as N-nitrosodimethylamine (NDMA), which are common in Minnesota surface waters. Additional outcomes of this project were promotion of Minnesota's human capital through training of graduate and undergraduate students (2 graduate and one undergraduate student were supported at various points of the project), a M. S. thesis completed by Henry Croll (one of the graduate students supported by the project), a conference presentation (at the Annual Meeting of the American Institute of Chemical Engineers, AIChE 2017), and a recent publication in Separation and Purification Technology, a peer-reviewed international journal.

Project Results Use and Dissemination

This project accomplished the following dissemination outcomes

Peer-reviewed publications (1): H. Croll, A. Soroush, M. Pillsbury, and SRVC. "Graphene oxide surface modification of polyamide reverse osmosis membranes for improved N-nitrosodimethylamine (NDMA) removal". Separation and Purification Technology 210 (2019) 973–980

The article is available from the following link without a subscription until November 2, 2018:

<https://authors.elsevier.com/a/1XjGX4wbrSvhOh>

Conference papers (1): A. Soroush, H. Croll, and SRVC. "N-Nitrosodimethylamine (NDMA) Removal by Thin Film Composite Polyamide Reverse Osmosis Membranes". 2017 AIChE National Meeting, Minneapolis, MN. November 1st, 2017.

Dissertations (1): H. Croll. "Improvements to Polyamide Reverse Osmosis Membranes for Removal of Small, Uncharged, Hydrophilic Solutes". MS Thesis, University of Minnesota, 2018 (available from the UMN Libraries).



Environment and Natural Resources Trust Fund (ENRTF)

M.L. 2016 Work Plan

Date of Report: September 30, 2018

Final Report

Date of Work Plan Approval: June 7, 2016

Project Completion Date: September 30, 2018

Does this submission include an amendment request? no

PROJECT TITLE: Membrane-Based Process for Decentralized Drinking Water Production

Project Manager: Santiago Romero-Vargas Castrillón, Ph. D.

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Location: Statewide

Total ENRTF Project Budget:

ENRTF Appropriation: \$191,000

Amount Spent: \$70,540.53

Balance: \$120,459.47

Legal Citation: M.L. 2016, Chp. 186, Sec. 2, Subd. 04I

Appropriation Language:

\$191,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop a low-energy use, membrane-based treatment technology to produce drinking water locally from surface waters by removing heavy metals and contaminants of emerging concern, including pesticides and pharmaceuticals. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2019, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Membrane-based Process for Decentralized Drinking Water Production

II. PROJECT STATEMENT: Water pollution and water scarcity are two of the central problems of our time, even in regions such as Minnesota and the Upper Midwest, rich in water resources. Ensuring that sufficient water supplies are available to meet human and ecological needs will demand sustainable water management, and novel technologies to treat water bodies impacted by contamination. In Minnesota, our ground and surface waters (i.e., rivers and lakes) exhibit increasing levels of contaminants such as heavy metals, pharmaceuticals, hormones, and personal care products, which are removed to an insufficient extent by conventional water treatment processes. There is thus a clear need to develop water treatment processes that minimize the potential for human exposure to these emerging contaminants. The objective of the proposed work is to develop a membrane-based water treatment process capable of producing potable water from untreated surface, well or ground water impacted by contaminants of emerging concern. The concept proposed combines two emerging membrane processes, forward osmosis (FO) and membrane distillation (MD), which can leverage solar thermal energy, geothermal energy, or industrial waste heat as energy sources. Therefore, the proposed process has the potential to be less energy intensive than reverse osmosis (RO) water treatment processes, while exhibiting comparable, if not higher, contaminant removal. Moreover, given that both FO and MD operate at around ambient pressures, the hybrid FO-MD process proposed will also show lower capital costs compared to RO; lower capital costs make the proposed technology an attractive option for decentralized water treatment in virtually any small community in Minnesota. The proposed effort is structured along the following objectives:

- Development of membrane distillation and forward osmosis membrane materials exhibiting high flux ($>12 \text{ gal ft}^{-2} \text{ day}^{-1}$) and high removal ($>90\%$) of contaminants commonly found in Minnesota surface and groundwater.
- Proof of concept demonstration of a hybrid FO-MD pilot-scale unit to produce drinking water from untreated surface or groundwater. The process developed will be scalable and its MD stage will operate at temperatures $< 80 \text{ }^\circ\text{C}$ ($< 176 \text{ }^\circ\text{F}$), such that low-grade heat may be used as the main energy supply for the process.

Amendment request (6/30/2018)

The project manager (PM) will be resigning from his position on the faculty at the University of Minnesota on September 30th, 2018. On consultation with Becca Nash, LCCMR director, it was recommended that the project completion date be changed to September 30th, 2018, upon which a final report will be submitted with the project findings. Further, it was recommended that student support be terminated at the end of the summer term (August 26th, 2018); this will allow the graduate student funded by this project to complete his research and manuscript submitted for publication. To reflect the changes to the project duration, the PM requests that the project completion date be changed to September 30th, 2018. Further, given that an alternate project manager could not be found, the PM requests that Activity 2 outcomes not be achieved and the funds remaining for that activity be returned to the ENRTF. The dataset for this project will remain at the University of Minnesota and will be included as an addendum to the dissertation and stored in the UMN library system. All capital equipment acquired through this project will be transferred to the Department of Civil, Environmental, and Geo-Engineering at the University of Minnesota in order to meet LCCMR requirements related to purchase of capital equipment. Further, the PM requests approval to transfer \$503 from personnel wages and benefits to supplies and services, given that the latter category was slightly overspent.

Amendment Approved by LCCMR 7/26/2018

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of January 30, 2017:

Work in the fall of 2016 focused on graduate student training, FO membrane development and the construction of a membrane testing apparatus. Details are provided in the status update of activity 1.

Project Status as of June, 30 2017:

Work in the spring of 2017 continued to focus on graduate student training, membrane synthesis, and troubleshooting of the membrane testing apparatus (which became fully operational in March of 2017).

Project Status as of January 30, 2018:

A membrane modification protocol was developed to improve the rejection of nitrosamines by water treatment membranes. A conference paper was presented reporting the results (see Dissemination). Note: expenses are reported in the appended spreadsheet through 12/31/17.

Project Status as of June 30, 2018:

We are currently developing membrane surface modification strategies to improve removal of urea, a contaminant that is commonly found in domestic wastewater. A manuscript reporting improved removal of NDMA by GO-modified membranes will be submitted shortly.

Overall Project Outcomes and Results:

The main outcome of this project is a novel surface modification protocol for water treatment membranes. We showed that graphene oxide coatings, known to exhibit antibacterial properties, improve the efficiency with which the membranes remove micropollutants, such as N-nitrosodimethylamine (NDMA), which are common in Minnesota surface waters. Additional outcomes of this project were promotion of Minnesota's human capital through training of graduate and undergraduate students (2 graduate and one undergraduate student were supported at various points of the project), a M. S. thesis completed by Henry Croll (one of the graduate students supported by the project), a conference presentation (at the Annual Meeting of the American Institute of Chemical Engineers, AIChE 2017), and a recent publication in *Separation and Purification Technology*, a peer-reviewed international journal.

Note: the student salary budget in activity 1 was slightly overspent by \$1882.46; to make up for this shortfall, \$1882.46 were moved from the student support budget of activity 2 to activity 1.

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Development of membrane materials for filtration by forward osmosis and membrane distillation

Forward osmosis is an emerging membrane process in which permeation is driven by osmotic pressure, i.e., the tendency of water to migrate across a selective membrane from a low-salinity solution to one of higher salinity. In the first stage of the proposed process, FO will be used to extract water from untreated surface waters into a synthetic salt solution known as draw solution. To achieve this goal, we will develop aromatic polyamide forward osmosis (FO) membranes. The FO membranes will be prepared by molecular layer-by-layer (mLBL) deposition, which will allow us to optimize the permeate water flux and the efficiency with which the membranes reject organic contaminants and heavy metals. The mLBL technique will also allow us to control the surface chemistry of the membrane, thereby enabling chemical modification with fouling-resistant coatings. Surface modification is essential to prevent membrane fouling (i.e., clogging) with natural organic matter and other compounds abundant in surface and ground waters.

The second stage of the proposed process leverages membrane distillation to separate purified water from the draw solution. In MD, thermal energy is supplied to the draw solution in order to drive pure water vapor across a

microporous hydrophobic membrane. Because temperatures around 60-80 °C suffice to drive permeation, low grade heat from solar, geothermal, or industrial sources can be used as energy supply for the separation process.

The FO and MD membrane materials will be characterized in terms of their water transport properties and solute rejection (using heavy metals such as Cd, and small organic molecules as model contaminants of emerging concern) using RO, FO and MD experimental setups. After optimization of the membrane materials with respect to water permeability, salt rejection, and fouling resistance, we will construct a lab-scale apparatus (membrane area approximately 20 cm²) to provide a proof-of-concept demonstration of a hybrid FO-MD water treatment process. The lab-scale prototype will be evaluated with a “synthetic” feed water with a composition representative of river and lake waters, as well as with feed waters sampled from the Mississippi River, Upper Red Lake, and Lake Superior.

Summary Budget Information for Activity 1:

ENRTF Budget: \$108,818.46
Amount Spent: \$70,540.53
Balance: \$38,277.93

Outcome	Completion Date
1. Personnel training and construction of lab-scale FO, RO and MD filtration setups	December 31, 2016
2. Initial FO membranes prepared by mLBL deposition	June 30, 2017
3. Initial MD membranes fabricated by phase inversion	June 30, 2017
4. Characterization and optimization of FO and MD membrane transport and selectivity properties	October 31, 2017
5. Characterization of FO and MD membrane fouling resistance	December 31, 2017
6. Proof-of-concept demonstration of a lab-scale hybrid FO-MD process, operating at < 80 °C, water flux of 20 L m ⁻² h ⁻¹ (12 gal ft ⁻² day ⁻¹), and showing >90% rejection of contaminants.	April 30, 2018

Activity Status as of January 30, 2017:

A laboratory-scale reverse osmosis (RO) setup was constructed in the lab of the PI. A graduate student is undergoing training in the synthesis of thin film composite forward osmosis membranes. Membrane synthesis by molecular layer-by-layer deposition has begun. The graduate student has also been trained in various experimental techniques required for materials characterization (atomic force microscopy, electron microscopy, zeta potential, IR spectroscopy, contact angle goniometry).

Activity Status as of June 30, 2017:

Work in the spring semester focused on Activity 1, specifically the development of FO membranes for drinking water treatment. The graduate student continued to be trained in membrane fabrication by non-solvent induced phase inversion (a technique that will also be used in the fabrication of distillation membranes), molecular layer-by-layer deposition, interfacial polymerization, and layered interfacial polymerization. In addition, an analysis protocol to measure the concentration of contaminants present in drinking water by LC-MS-MS was developed. This protocol is currently being used to measure the removal of contaminants with the fabricated membranes. In addition, we are exploring the fabrication of membranes with novel monomers to improve the removal of drinking water contaminants.

Activity Status as of January 30, 2018:

We modified polyamide membranes for water treatment with graphene oxide (GO), a carbon-based nanomaterial. GO is usually added to membrane surfaces to improve their resistance to biofouling. However, we found that, in addition to this, GO improves the removal of NDMA, a carcinogenic disinfection byproduct

common in drinking water sources. The rejection of NDMA by GO-modified membranes was found to be 5% higher than that of unmodified membranes (i.e., 82.5% compared to 77.1%). In addition, the permselectivity of the membranes, defined as the ratio of the water permeability to that of NDMA, was also found to be higher after modification of the membranes with GO: for GO-modified membranes it was found to be 492, whereas for GO-free membranes a permselectivity of 370 was found.

These results were presented during a national chemical engineering conference (see Dissemination). A manuscript reporting these findings will also be prepared for submission to a scholarly journal.

Activity Status as of June 30, 2018:

We are currently developing membrane surface modification protocols for removal of low-molecular weight contaminants, such as urea. The surface modification currently being investigated consists of grafting fluorinated alkylamines to the membrane surface using EDC-NHS coupling chemistry.

A manuscript reporting the improved removal of NDMA by GO-functionalized membranes (see 1/30/18 status update) was written and will be submitted shortly.

Project Outcomes and Results: As explained below, a novel functionalization of the membrane surface improved the rejection of nitrosamines, which are carcinogenic compounds generated during disinfection of water and wastewater.

Final Report Summary: In the growing area of membrane-based water treatment, the performance of reverse osmosis (RO) is limited by poor membrane selectivity towards nitrosamines and other low-molecular weight, neutral contaminants, some of which affect Minnesota’s rivers and lakes. This study aimed to increase RO membrane rejection of N-nitrosodimethylamine (NDMA), a carcinogenic nitrosamine that is produced during chlorination and chloramination of secondary wastewater effluent. Toward this goal, we modified commercial polyamide RO membranes with graphene oxide (GO) nanosheets, and demonstrated that GO functionalization can decrease the NDMA permeability coefficient by 31%, while only decreasing water permeability by 13%. The improved selectivity is likely due to additional steric exclusion derived from the GO nanosheet coating. Moreover, membrane characterization indicated that the GO modification does not change the hydrophilicity or roughness of the interface. The latter interfacial characteristics, combined with the well-established biocidal properties of graphenic nanomaterials, render GO functionalization a promising strategy for the development of highly selective membranes for water treatment and wastewater reclamation.

Activity 2: Development of a pilot-scale hybrid FO-MD water purification process. The prototype developed in Activity 1 will be scaled up to a membrane area of 150 cm² (0.16 ft²). The performance metrics that will be considered to assess the success of the pilot-scale unit are a production rate of 2 gal/day with < 10% flux decrease due to fouling over 24 hours of operation, and >90% removal of organic contaminants and heavy metals. In addition, the MD stage of the pilot will operate a temperatures < 80 °C. Experiments will be conducted with feed waters collected from the Mississippi River, Upper Red Lake, and Lake Superior.

Summary Budget Information for Activity 2:

ENRTF Budget: \$82,181.54
Amount Spent: \$ 0
Balance: \$82,181.54

Outcome	Completion Date
1. Pilot-scale construction	April 30, 2018
2. Initial characterization of water flux and contaminant rejection in pilot-scale unit	December 31, 2018
3. Demonstration of pilot-scale unit showing >90% contaminant rejection at temperatures < 80 °C	June 30, 2019

Activity Status as of January 30, 2017: no activity to report

Activity Status as of June 30, 2017: no activity to report

Activity Status as of January 30, 2018: no activity to report

Activity Status as of June 30, 2018: no activity to report. Due to the circumstances discussed in the June 30, 2018 amendment request, this activity will not continue and the funds will be returned to the ENRTF after project close-out.

Project Outcomes and Results: no activity to report

Final Report Summary: no activity to report

V. DISSEMINATION:

Description: Results will be disseminated via publication in peer-reviewed journals such as The Journal of Membrane Science, Water Research, and Environmental Science & Technology. Results will also be communicated through oral and poster presentations at local, regional and national conferences on water technology.

Status as of January 30, 2017: no activity to report

Status as of June 30, 2017: no activity to report

Status as of January 30, 2018: the graduate student presented a paper at the 2017 AIChE National Meeting in Minneapolis, on November 1st, 2017. The title of the presentation was:
“N-Nitrosodimethylamine (NDMA) Removal by Thin Film Composite Polyamide Reverse Osmosis Membranes”

Status as of June 30 2018: no activity to report

Final Report Summary: This project accomplished the following dissemination outcomes

Peer-reviewed publications (1): H. Croll, A. Soroush, M. Pillsbury, and SRVC. “Graphene oxide surface modification of polyamide reverse osmosis membranes for improved N-nitrosodimethylamine (NDMA) removal”. Separation and Purification Technology 210 (2019) 973–980

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Conference papers (1): A. Soroush, H. Croll, and SRVC. “N-Nitrosodimethylamine (NDMA) Removal by Thin Film Composite Polyamide Reverse Osmosis Membranes”. 2017 AIChE National Meeting, Minneapolis, MN. November 1st, 2017.

Dissertations (1): H. Croll. “Improvements to Polyamide Reverse Osmosis Membranes for Removal of Small, Uncharged, Hydrophilic Solutes”. MS Thesis, University of Minnesota, 2018. (available from the UMN Libraries)

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	\$ Amount	Overview Explanation
Personnel:	\$86,892	Graduate research assistant (50% time per year for two years, salary 57% of cost, tuition 33% of cost, fringe benefits 10% of cost)
Professional/Technical/Service Contracts:	\$N/A	
Equipment/Tools/Supplies:	\$21,767	Laboratory equipment and supplies (\$21,264) including, but not limited to: chemicals for membrane fabrication and characterization (polysulfone, poly(ether sulfone), poly(vinyl pyrrolidone) and poly(vinylidene fluoride), polyethylene glycol, dopamine hydrochloride, Tris HCl buffer, ethylenediamine, m-phenylene diamine, trimesoyl chloride, n-hydroxysuccinimide, EDC carbodiimide), alginate, bovine serum albumin, Suwanee River natural organic matter, organic solvents for membrane fabrication (dimethylformamide, n-methyl-pyrrolidinone, acetone, ethanol, isopropanol, iso-par-g, hexane), membrane casting equipment (casting blade, non-woven fabric, glass plates), supplies for membrane characterization (microscopy sample holders and cantilevers for force spectroscopy), characterization facility user fees (for use of analytical instrumentation in the Characterization Facility at UMN).
Capital Expenditures over \$5,000:	\$81,341	Spin coater for membrane fabrication (\$8,000), lab-scale forward osmosis (FO) apparatus (\$15,000), lab-scale membrane distillation (MD) apparatus (\$15,000), lab-scale reverse osmosis (RO) apparatus (\$15,041), pilot-scale hybrid FO-MD unit (\$28,300).
Travel Expenses in MN:	\$ 1,000	Travel in Minnesota for surface water collection such as Lake Superior and Upper Red Lake. Mileage will be reimbursed at \$0.55 per mile or current UMN compensation plan.
TOTAL ENRTF BUDGET:	\$ 191,000	

Explanation of Use of Classified Staff: N/A

Explanation of Capital Expenditures Greater Than \$5,000:

Spin coater for forward osmosis membrane fabrication (\$8,000): a spin coater is necessary for the fabrication of forward osmosis membranes using the molecular layer-by-layer deposition technique.

Lab-scale forward osmosis (FO, \$15,000), membrane distillation (MD, \$15,000) and reverse osmosis (RO, \$15,041) units: one lab-scale FO and one lab-scale MD unit are required to characterize the water transport properties (i.e., water permeability) of the FO and MD membrane materials developed in activity 1, as well as the fouling resistance of the materials. A RO lab-scale unit is needed to determine the solute permeability coefficient of the membranes developed in activity 1. Components for the construction of 1 lab-scale forward osmosis and 1 membrane distillation system: Gear pumps, heads and water heater/chiller (8 pumps, 2

heaters/chillers, total: \$17,000), custom-made flow cells for forward osmosis and membrane distillation (2 cells, total: \$2,000), unit instrumentation (2 computers, 2 conductivity meters, 4 stirring plates, 8 flowmeters, valves, fittings, water reservoirs, total: \$11,000). Components for the RO setup: high pressure pump (\$10,641), filtration cell (\$1,000), valves, tubing, fittings, flowmeters (\$3400).

Fabrication of a pilot-scale FO-MD water purification system as part of activity 2 (\$28,300): filtration cells (2 @ \$2500 each), 1 heater unit (\$4300), 1 chiller (\$3000), 4 gear pumps and 4 pump drives (\$6,000), tubing, valves, instrumentation (\$10,000).

Per the June 30, 2018 amendment request, all capital equipment will be transferred to the Department of Civil, Environmental, and Geo- Engineering at the University of Minnesota so it can continue to be used for its useful life for the intended purpose or, if the use changes, to pay back the Environment and Natural Resources Trust Fund an amount equal to either the cash value received or a residual value approved by the LCCMR director if it is sold.

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: A full-time graduate student researcher will be employed with this appropriation for 2 years (for 2 FTE over the entire 3-year project period). This results in a total of 1 FTE for the total project.

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: N/A

B. Other Funds:

Source of Funds	\$ Amount Proposed	\$ Amount Spent	Use of Other Funds
Non-state			
N/A	N/A	N/A	N/A
State	N/A	N/A	N/A
	\$	\$	
TOTAL OTHER FUNDS:	\$N/A	\$N/A	

VII. PROJECT STRATEGY:

A. Project Partners:

The project manager will be Professor Santiago Romero-Vargas Castrillón (U. of Minnesota), who will supervise a graduate student in the execution of the proposed work. Romero-Vargas has expertise in the development, characterization, and testing of membrane materials for water purification, and membrane-based processes for water production.

B. Project Impact and Long-Term Strategy:

The proposed work will result in membrane materials and low-energy processes for the removal of heavy metals and organic contaminants of emerging concern from untreated surface waters in Minnesota. We expect this project to lead to further applications in municipal wastewater treatment (e.g., the direct, decentralized treatment of sewage) and, also, to patentable technology.

C. Funding History:

Funding Source and Use of Funds	Funding Timeframe	\$ Amount
United States Geological Survey. Project title: "Improving the (Bio)fouling and Mechanical Resistance of Ultrafiltration Membranes for Drinking Water Production". The project proposed in this work plan partially builds on results and expertise developed during the USGS-sponsored project.	3/1/2015 – 2/28/2016	\$ 30,000

Matching funds from UMN for the abovementioned USGS project.	3/1/2015 – 2/28/2016	\$60,000
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VIII. FEE TITLE ACQUISITION/CONSERVATION EASEMENT/RESTORATION REQUIREMENTS:

A. Parcel List: N/A

B. Acquisition/Restoration Information: N/A

IX. VISUAL COMPONENT or MAP(S):

See attached.

X. RESEARCH ADDENDUM:

See attached.

XI. REPORTING REQUIREMENTS:

Periodic work plan status update reports will be submitted no later than January 30, 2017, June 30, 2017, January 30, 2018, and June 30, 2018. A final report and associated products will be submitted by September 30th, 2018.

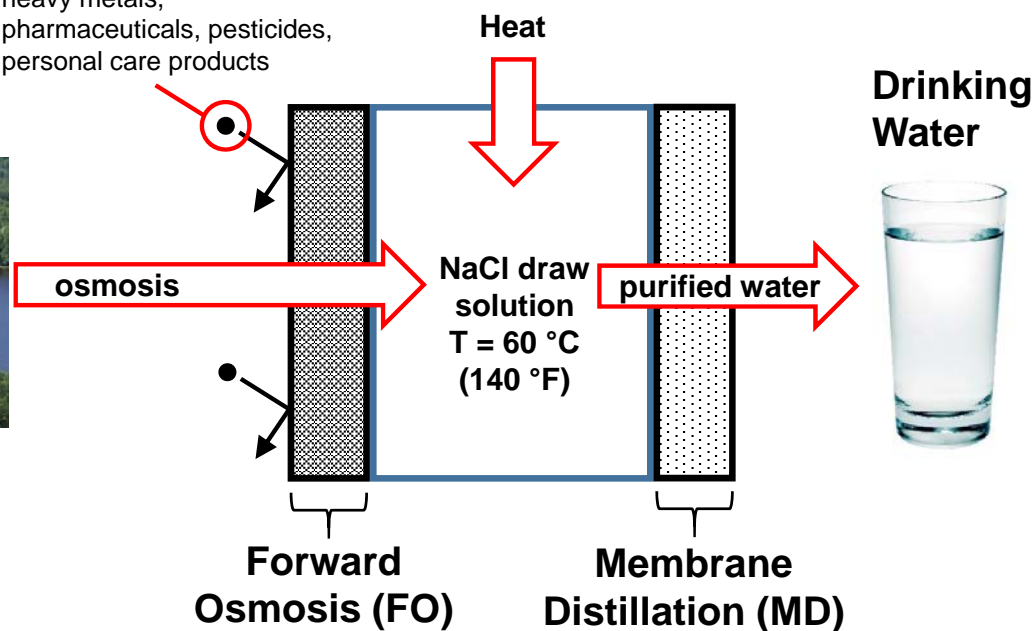
Spin coater for forward osmosis membrane fabrication: a spin coater is necessary for the fabrication of membranes using the molecular layer-by-layer technique	\$8,000.00	\$0.00	\$8,000.00	\$0.00	\$0.00	\$0.00	\$8,000.00	\$8,000.00
Fabrication of one bench-scale forward osmosis experimental setup and one membrane distillation experimental setup: a bench-scale setup to be used for membrane characterization and fouling experiments during activity 1 of the project. Components for the construction of 1 lab-scale forward osmosis and 1 membrane distillation system: Gear pumps, heads and water heater/chiller (8 pumps, 2 heaters/chillers, total: \$17000), custom-made flow cells for forward osmosis and membrane distillation (2 cells, total: \$2000), unit instrumentation (2 computers, 2 conductivity meters, 4 stirring plates, 8 flowmeters, 8 3-way valves, 2 10-packs of fittings, 4 water reservoirs, total: \$11000).	\$30,000.00	\$0.00	\$30,000.00	\$0.00	\$0.00	\$0.00	\$30,000.00	\$30,000.00
Fabrication of a reverse osmosis experimental setup for the characterization of membranes: high pressure pump (\$10,641), filtration cell (\$1,000), valves, tubing, fittings, flowmeters (\$3400).	\$15,041.00	\$14,763.07	\$277.93	\$0.00	\$0.00	\$0.00	\$15,041.00	\$277.93
Fabrication of a pilot-scale FO-MD water purification system as part of activity 2: filtration cells (2 @ \$2500 each, 1 heater unit @ \$4300, 1 chiller @ \$3000, 4 gear pumps and 4 pump drives @ \$6,000, tubing, valves, instrumentation @ \$10,000)	\$0.00	\$0.00	\$0.00	\$28,300.00	\$0.00	\$28,300.00	\$28,300.00	\$28,300.00
Travel expenses in Minnesota								
Mileage and lodging. To collect water samples within Minnesota (Lake Superior, Upper Red Lake, Mississippi River). Mileage will be reimbursed @ \$0.55 per mile or current U of M compensation plan.		\$0.00	\$0.00	\$1,000.00	\$0.00	\$1,000.00	\$1,000.00	\$1,000.00
COLUMN TOTAL	\$108,818.46	\$70,540.53	\$38,277.93	\$82,181.54	\$0.00	\$82,181.54	\$191,000.00	\$120,459.47

Membrane-based process for decentralized drinking water production.

Untreated
Surface Water
(lakes, rivers,
groundwater)



heavy metals,
pharmaceuticals, pesticides,
personal care products





Graphene oxide surface modification of polyamide reverse osmosis membranes for improved *N*-nitrosodimethylamine (NDMA) removal

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ARTICLE INFO

Keywords:

Reverse osmosis
Wastewater reuse
N-nitrosodimethylamine
Graphene oxide
Polyamide

ABSTRACT

In the growing area of wastewater reuse, the performance of reverse osmosis (RO) is limited by poor membrane selectivity towards nitrosamines and other low-molecular weight, neutral contaminants. This study aimed to increase RO membrane rejection of *N*-nitrosodimethylamine (NDMA), a carcinogenic nitrosamine that is produced during chlorination and chloramination of secondary wastewater effluent. Toward this goal, we modified commercial polyamide RO membranes with graphene oxide (GO) nanosheets, and demonstrated that GO functionalization can decrease the NDMA permeability coefficient by 31%, while only decreasing water permeability by 13%. The improved selectivity is likely due to additional steric exclusion derived from the GO nanosheet coating. Moreover, membrane characterization indicated that the GO modification does not change the hydrophilicity or roughness of the interface. The latter interfacial characteristics, combined with the well-established biocidal properties of graphenic nanomaterials, render GO functionalization a promising strategy for the development of highly selective membranes for wastewater reclamation.

1. Introduction

Water scarcity is a central problem of our time. Millions of people are affected by difficult or intermittent access to drinking water, a problem that will be aggravated by population growth, industrialization, urbanization and climate change [1]. With less than 1% of available water supply in the form of drinking water, there is a clear need for technologies capable of tapping unconventional water sources (e.g., brackish water, seawater, and wastewater) [2] to augment the water inventory beyond what is available from the hydrological cycle. Given their relatively low energy requirements and high pollutant removal, membrane-based processes such as reverse osmosis (RO) hold significant promise in augmenting our water supply through seawater desalination and advanced wastewater treatment [2].

The inception of the thin film composite (TFC) membrane contributed significantly to the decrease in the energy consumption of desalination and wastewater reclamation by RO [1,2]. TFC membranes [3] display high contaminant rejection (> 99% for ionic species, as well as a wide variety of micropollutants with molecular weight ≥ 150 Da [2]), and high water permeability ($2\text{--}5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ [2]) owing to a thin ($\sim 200\text{--}300 \text{ nm}$ [4]) polyamide selective layer. Conventional polyamide TFC membranes are fabricated by interfacial polymerization

(IP) of aromatic amines and acyl chlorides, typically *m*-phenylene diamine in aqueous solution and trimesoyl chloride dissolved in organic, apolar solvents [1,3,5,6]. Because IP is a stochastic, self-limiting process [5,6], the resulting active layer is a highly crosslinked glassy polymer whose chemical composition and morphology are difficult to control, and whose selectivity has proven challenging to improve. Consequently, state-of-the-art RO membranes are permeable to small, hydrophilic neutral solutes (SNSs) (i.e., those with a molecular diameter similar to that of a water molecule, $\sim 0.3 \text{ nm}$), many of which are toxic [2,7–9]. Examples of SNSs which show low rejection include boron, arsenic and a host of organic disinfection byproducts (DBPs) [2,10]. The environmental and health impacts of these species range from damage in crops to cancer and developmental/reproductive effects in humans [11].

Among SNSs, the National Research Council identified *N*-nitrosodimethylamine (NDMA) (a byproduct of chloramination of secondary wastewater effluent [12,13]) as significantly concerning due to its being a potent carcinogen [14]. Different countries and regions have adopted recommendations about the presence of NDMA in drinking water: California has adopted a notification goal of 10 ng L^{-1} for NDMA and other nitrosamines [15,16], while Germany and the Netherlands have adopted guide values of 10 and 12 ng L^{-1} , respectively, for NDMA

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[16]. Concerning wastewater effluent, the regulatory level for NDMA in Ontario is 200 ng L^{-1} [16]. Owing to its small molecular radius (0.248 nm [9]), hydrophilicity ($\log K_{\text{ow, NDMA}} = -0.57$, where K_{ow} is the 1-octanol/water partition coefficient [17]), and uncharged state at pH 6–8 [15], NDMA is sparsely removed by conventional membranes, with observed rejection coefficients in the 5–80% range for brackish water RO membranes [15]. Such rejection results in low RO permeate quality when the feed is impacted with wastewater disinfected with chloramines [18]. Removal of NDMA thus requires an expensive advanced oxidation process (AOP) downstream of the RO stage to degrade NDMA to less toxic compounds [2,14]. Development of a high rejection membrane would therefore reduce the capital and operating costs of advanced reuse processes, in addition to producing safer reclaimed water.

Previous research has found a strong correlation between the minimum projected area of NDMA and other neutral solutes, and their rejection by RO membranes [4], suggesting that steric hindrance derived from sub-nanometer voids in the selective layer influences contaminant transport and selectivity. Accordingly, efforts to improve the rejection of NDMA and other SNSs (e.g., boric acid) have focused on reducing the void-volume fraction through heat treatment [15,19], or via surface modification of the polyamide layer with aliphatic alkylamines [20] or monomers such as glycidyl methacrylate [7], that reduce void-volume size and disrupt solute-solvent hydrogen bonding [7,20,21]. However, the chemical moieties used in these modifications are hydrophobic [7,20], resulting in a polyamide surface with possible high organic and biological fouling propensity. Membrane surface modification with biocidal nanomaterials such as graphene oxide (GO) has proven effective in mitigating biofouling [22–24]. If, in addition, GO surface coatings could improve NDMA rejection, a valuable synergy for wastewater reuse membranes would result. However, to-date, the effect of nanomaterial surface coatings on the rejection of SNSs such as NDMA by polyamide membranes has not been explored.

In this paper we investigate the impact of GO modification on the rejection of NDMA in RO membrane filtration. We show that modifying commercial RO membranes with a GO surface coating can improve the rejection of NDMA by 6% (equivalent to a decrease in NDMA permeability coefficient of 31%) and the water/NDMA permselectivity (ratio of the permeability coefficients of water and NDMA) by 43%. The higher rejection of NDMA by GO-modified membranes is attributed to sealing of polyamide defects by GO nanosheets.

2. Materials and methods

2.1. Graphene oxide synthesis and characterization

Graphene oxide (GO) was prepared by chemical exfoliation of graphite (Bay Carbon, SP-1, 325 mesh) following the modified Hummers method [25]. A detailed description of the synthesis and material characterization can be found in our previous publication [26]. GO nanosheets were readily dispersible in ultrapure water (18.2 M Ω cm, Barnstead) and exhibited a mean lateral dimension (determined from scanning electron micrographs) of ~ 80 nm and thickness of ~ 1 nm (measured by tapping mode AFM), consistent with single-layer GO nanosheets [27]. Raman spectroscopy confirmed the presence of the graphite lattice in-phase vibration (G) band at $\sim 1590 \text{ cm}^{-1}$ and the disorder (D) band at $\sim 1350 \text{ cm}^{-1}$ [28].

2.2. Surface modification with graphene oxide (GO)

Polyamide thin-film composite RO membranes (SW30HR, Dow Water & Process Solutions) were provided as flat sheets and stored dry until use. Given their high rejection of other SNSs (e.g., boric acid [7,21]), seawater RO (SWRO) membranes such as SW30HR constitute a suitable material platform with which to investigate DBP removal. Before surface modification, membrane coupons were immersed in 25%

aqueous isopropanol for 30 min, and then rinsed in ultrapure water for 1 h. To functionalize the membrane surface with GO, we adapted the protocol developed by Perreault et al. [22], according to which nanosheets are tethered to polyamide via amine coupling chemistry [29] using an ethylenediamine (ED, BioXtra, Sigma) linker. Briefly, carboxylic acid groups on the polyamide active layer are converted to amine-reactive esters using EDC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, 98%, Sigma) and NHS (*N*-hydroxysuccinimide, 98%, Sigma), at concentrations of 4 mM and 10 mM, respectively, in a 10 mM MES buffer solution (MES monohydrate, BioXtra, 99%, Sigma), pH 5.0, containing 0.5 M NaCl. After 60 min, the membrane is washed with ultrapure water and contacted with a 10 mM ED solution in 10 mM HEPES buffer (99.5%, Sigma), pH 7.5, containing 0.15 mM NaCl for 30 min; this step functionalizes the membrane surface with primary amine groups through reaction of ED with the activated esters. To activate the GO suspension, 10 parts of $250 \mu\text{g mL}^{-1}$ GO suspension is combined with 2 parts 100 mM MES buffer, which is mixed with 1.75 parts 20 mM EDC (in 10 mM MES buffer) followed by 1.75 parts 50 mM NHS (in 10 mM MES buffer) to convert carboxylic acid groups that decorate the GO nanosheet edges into amine-reactive esters. The pH of EDC-NHS-activated GO dispersion is adjusted to 5.5, and after 15 min it is increased to 7.2 by the addition of NaOH dropwise. The ED-functionalized membrane is then exposed to the activated GO dispersion for 60 min, allowing reaction of the activated GO with the primary amine groups present on the membrane surface. Finally, the membrane is bath sonicated for 5 min to remove adsorbed GO, and stored at approximately 4°C in ultrapure water until use. All membrane modifications were performed at room temperature in an orbital shaker at 30 rpm. Membrane coupons were mounted between a polypropylene backing and a PTFE frame, leaving only the polyamide active layer exposed to the modification solutions.

2.3. Characterization of membrane chemistry and interfacial properties

2.3.1. Conformal Raman mapping

Raman spectroscopy (Witec Alpha300R) was used to verify the presence and characterize the spatial distribution of GO nanosheets on the polyamide surface. Raman maps were determined over $20 \times 20 \mu\text{m}^2$ scan areas on desiccator-dried membranes at $0.5 \mu\text{m}$ resolution, measuring 4 spectra per square micron. To generate the GO surface density maps, we computed the ratio of the areas under the D band of GO and the polysulfone C–O–C stretching band (observed at $\sim 1150 \text{ cm}^{-1}$ [22,30]) derived from the RO membrane support.

2.3.2. Scanning electron and atomic force microscopy

Membrane surface morphology was characterized by field emission scanning electron microscopy (FESEM). The samples were sputter-coated with 5 nm of iridium (Leica EM, ACE 600) to enable SEM imaging (Hitachi SU8230). Membrane surface topography was characterized by tapping mode AFM in air using a MFP-3D-Bio AFM (Asylum Research), with AC160TS-R3 probes (Asylum Research, nominal $k = 26 \text{ N/m}$). Surface images were collected at 0.5 Hz over $2.5 \times 2.5 \mu\text{m}^2$ areas. Root-mean-square (RMS) roughness was calculated from five AFM scans of different specimens for each membrane type.

2.3.3. Contact angle goniometry

Membrane surface hydrophobicity was characterized by the contact angle of *n*-decane droplets suspended in ultrapure water. The captive droplet technique allows investigation of membrane hydrophobicity in aqueous environments and circumvents artifacts due to membrane drying [31]. A goniometer (Ramé-Hart, Model 200) was used to determine the contact angles of *n*-decane droplets ($\sim 10 \mu\text{L}$ volume) injected with a J-shaped needle into a fluid cell containing ultrapure water. DROP Image software (Ramé-Hart) was used to measure the contact angle of each droplet. For each membrane type, two replicate

specimens were measured for a total of 12 *n*-decane droplets.

2.3.4. Streaming potential measurements

The zeta potential of the membrane surface was determined from streaming potential measurements using an electrokinetic analyzer (SurPASS, Anton-Paar). Two membrane coupons were affixed to the sample holders of an adjustable gap cell with a gap size of 120 μm . The streaming potential was measured in 1 mM KCl from pH 10 to pH 4, adjusted with aliquots of 0.05 M HCl. The zeta potential was computed from the measured streaming potential using the Smoluchowski-Helmholtz equation [32]. For each membrane type, two separate membrane specimens were characterized.

2.4. NDMA removal efficiency

2.4.1. Analytical techniques

Samples of feed and permeate solutions were analyzed by capillary LC ESI⁺-MS/MS with a TSQ Vantage triple quadrupole (Thermo Scientific) interfaced to a Dionex Ultimate 3000 rapid separation LC (RSLC) high performance liquid chromatography (HPLC) system (Thermo Scientific) to measure the relative amount of NDMA present in filtered water samples. Chromatographic separation was achieved using an Agilent Zorbax SB-C18 5 μm , 150 mm \times 0.5 mm column. Samples were eluted at a flow rate of 15 $\mu\text{L}/\text{min}$ at room temperature using 2 mM ammonium acetate with 0.1% formic acid in water and methanol with 0.1% formic acid as buffers. The column was run under isocratic conditions at 10% methanol for 9 min. NDMA elutes from the column at 4.35 min and was monitored by the selected reaction monitoring (SRM) transitions $m/z = 75.08 \rightarrow 43.13$ and $75.08 \rightarrow 58.17$. Quantitation was based on $m/z = 43.13$, while $m/z = 58.17$ was used as a qualifier ion. The instrument was operated with an electrospray ionization source with a spray voltage of 3500 kV in positive ionization mode. Nitrogen was used as the sheath and auxiliary gas (20 and 0.5 units, respectively), and the ion transfer tube was set to 350 $^{\circ}\text{C}$. Argon was used as the collision gas, and set to 1.0 mTorr. For $m/z = 43.13$, a collision energy of 16 V was used, and for $m/z = 58.17$ a collision energy of 12 V was used. The S-Lens of the instrument was set to 40 V, and a declustering voltage of 10 V was used. Quadrupole resolution was achieved at 0.7 (FWHM) for both Q1 and Q3. A sample chromatogram is given in Fig. S1 of the Appendix. Prepared synthetic standards over the expected concentration range were injected to create a standard curve. Sample NDMA concentration was determined from the measured peak area using the standard curve.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.seppur.2018.08.070>.

2.4.2. Membrane filtration system

A laboratory-scale RO filtration apparatus was employed, consisting of a crossflow cell (CF042D, Sterlitech) with a membrane active area of 42.1 cm^2 , high-pressure pump (HydraCell M-03S, Wanner Engineering), 19-L stainless steel feed reservoir and heat exchange coil (Sterlitech) and chiller unit (6500 Series, PolyScience). The permeate flow rate was recorded by either a digital flow meter (SLI, Sensirion) connected to a computer, or by measuring the permeate volume as a function of time (in the latter case, good agreement was found with data recorded by the digital flow meter).

2.4.3. Characterization of NDMA rejection

Membranes were tested in ultrapure water supplemented with NDMA at a concentration of 890 $\mu\text{g L}^{-1}$ (dosed from a 1.35 M NDMA stock solution, prepared in water from neat NDMA (Supelco, Sigma Aldrich)). This elevated feed concentration was chosen because it facilitates direct analysis by LC-MS/MS without the need for sample concentration. Moreover, we carried out two additional experiments to investigate the effect of feed concentration on rejection with control membranes. Experiments at higher feed concentration (1125 $\mu\text{g L}^{-1}$, $R_{\text{NDMA}} = 84.9\%$) and lower feed concentration (462 $\mu\text{g L}^{-1}$, $R_{\text{NDMA}} = 82.2\%$) showed no apparent effect on NDMA removal, in agreement with previous work [33]. All experiments were conducted at a feed temperature of 22 $^{\circ}\text{C}$ and a crossflow velocity $u = 0.08 \text{ m s}^{-1}$. Under these conditions, $Re = ud_H/\nu = 363$, where $d_H = 4.38 \times 10^{-3} \text{ m}$ is the hydraulic diameter of the crossflow channel and ν is the kinematic viscosity of water at 22 $^{\circ}\text{C}$, equal to $9.57 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. The pH of the feed solution was ~ 5.8 – 6.2 , conditions under which NDMA is uncharged [15]. The permeate flux was first allowed to reach steady state by compacting the membrane at 400 psi with an ultrapure water feed. Following compaction, NDMA was dosed to the feed tank. After allowing at least 2 h for the solute to attain adsorption equilibrium with the membrane, 3 feed and 3 permeate samples were collected in 300 μL glass vials and stored in the dark at approximately 4 $^{\circ}\text{C}$ until analysis by LC-MS/MS was conducted.

The intrinsic water permeability (A) was determined by dividing the permeate flux (J_w) by the transmembrane pressure difference (Δp). NDMA separation was quantified by the rejection coefficient $R_{\text{NDMA}} = 1 - C_p/C_f$, where C_p and C_f are the bulk permeate and feed NDMA concentrations. Reported values of R_{NDMA} represent the average of three measurements. The permeability coefficient of NDMA (B) was computed from

$$B = J_w \left(\frac{1 - R_{\text{NDMA}}}{R_{\text{NDMA}}} \right) \exp \left(-\frac{J_w}{k} \right) \quad (1)$$

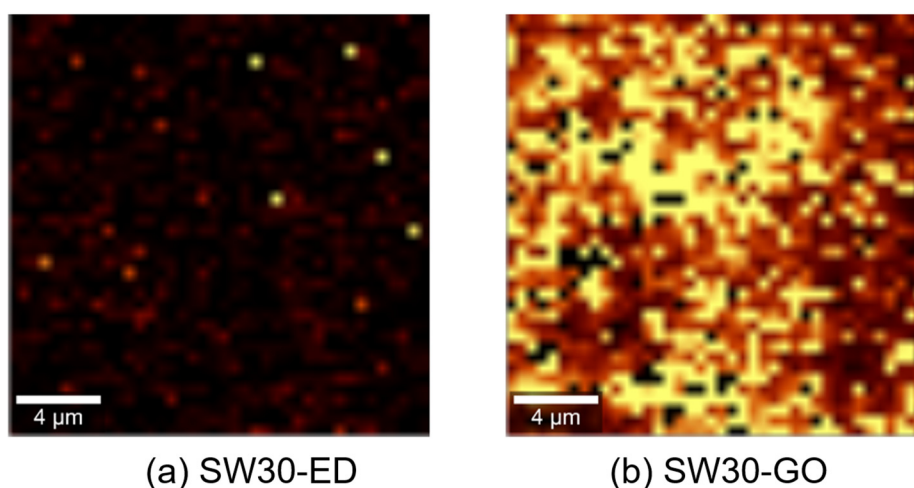


Fig. 1. Raman spectroscopy maps of (a) ethylenediamine (ED)-modified (SW30-ED) and (b) GO-functionalized (SW30-GO) polyamide membrane surfaces.

where k is the mass transfer coefficient, calculated from the correlation for the Sherwood number ($Sh = kd_H/D$, where $D = 9.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ is the aqueous diffusivity of NDMA [33]) under laminar flow in thin rectangular channels without spacers [34],

$$Sh = 1.85(ReSc_dH/L)^{0.33} \quad (2)$$

where $Sc = \nu/D$ is the Schmidt number and $L = 9.2 \times 10^{-2} \text{ m}$ is the length of the crossflow channel.

2.5. Statistical analysis

Homoscedastic (equal variance) unpaired t -tests were performed using Microsoft Excel to determine the statistical significance of the results. To evaluate the removal of NDMA by the different membrane materials, we considered seven membrane specimens independently functionalized with GO (hereinafter referred to as SW30-GO). In addition, we characterized NDMA rejection of six control membranes (designated as SW30), and two membranes functionalized with ED (designated SW30-ED). Error estimates in NDMA rejection coefficient are given as the standard deviation of three different measurements.

3. Results and discussion

3.1. Membrane material characterization

3.1.1. Raman spectroscopy and electron microscopy

We assessed the extent of membrane surface functionalization with GO by means of confocal Raman mapping. The results are presented in Fig. 1. The Raman map corresponding to the SW30-GO membrane (Fig. 1(b)) exhibits regions of high brightness (whose intensity is proportional to the ratio of the D band in GO to the polysulfone band), thus confirming successful functionalization with GO. The heterogeneity in the coverage observed in Fig. 1(b) is likely due to the broad sheet size distribution observed in the synthesized GO, with sheet lateral dimensions varying by one order of magnitude [26]. Conversely, no GO signatures are observed in the GO-free SW30-ED membrane (Fig. 1(a)).

Similarly, electron micrographs presented in Fig. 2 confirm the presence of GO as a crumpled sheet-like nanomaterial overlaying the polyamide (Fig. 2(b)), or as darker regions over the polyamide (Fig. 2(d)); these morphological features are absent in the SW30 control

(Fig. 2(a) and (c)), which shows the well-known leaf-like structure of polyamide [35]. The features noted in the micrographs of Fig. 2 are consistent with those reported previously by others in similar systems [22,23].

3.1.2. Interfacial properties

The effect of GO functionalization on surface roughness and membrane wettability is explored in Figs. 3 and 4, respectively, using atomic force microscopy (AFM) and contact angle goniometry. The AFM image corresponding to SW30 (Fig. 3(a)) exhibits the familiar ridge-and-valley structure of polyamide [5,36]. A seemingly different morphology is exhibited by the SW30-GO specimen (Fig. 3(b)), with smoother domains that are possibly due to GO nanosheets covering the rougher features of polyamide. These differences, however, are not reflected in the root-mean-squared roughness, which demonstrated similar values for both types of membranes: $60.2 \pm 9.7 \text{ nm}$ for SW30 and $58.8 \pm 7.3 \text{ nm}$ for SW30-GO ($p = 0.82$).

Fig. 4 presents results on the wettability of the membrane surfaces by a hydrophobic organic liquid, characterized by the contact angle of captive n -decane droplets in ultrapure water. With contact angles $> 90^\circ$ (measured through the n -decane droplet), the results show that both membrane interfaces were poorly wetted by n -decane. On closer inspection, we observe a slightly larger contact angle in SW30-GO (164.0° compared to 161.2° for SW30, $p = 0.008$), suggesting that GO surface modification results in a somewhat more hydrophilic interface compared to the control, a result that can be attributed to the hydrophilicity of GO films [26]. The results in Figs. 3 and 4 therefore show that GO functionalization does not render the membrane surface more hydrophobic nor does it increase surface roughness, both of which are desirable features from the point of view of fouling control [37,38].

To elucidate the effect of GO functionalization on membrane charge, we determined the ζ -potential of the membrane surfaces by means of streaming potential measurements. The results are presented in Fig. 5. Control (SW30) and ED-functionalized membranes (SW30-ED) exhibited no discernible differences in charging behavior in the pH 4–10 range, the surface charge becoming more negative as pH increases, due to deprotonation of carboxylic acid functional groups [39]. In contrast, a significant increase in surface charge was observed in SW30-GO membrane specimens, with the zeta potential increasing (in absolute value terms) by $\sim 25 \text{ mV}$ at circumneutral pH relative to the

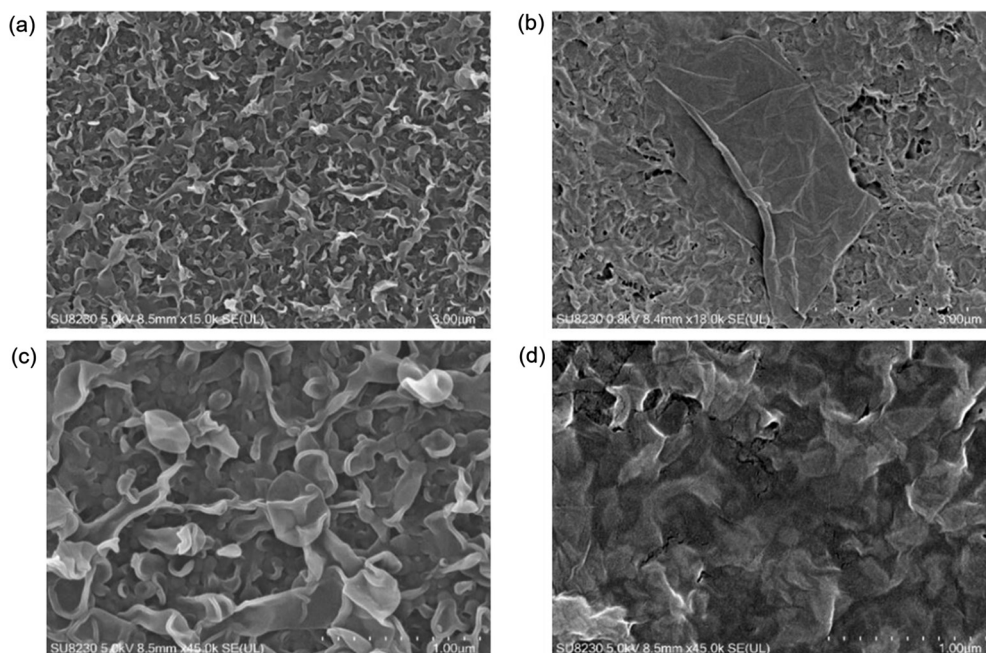


Fig. 2. Scanning electron micrographs of (a, c) control (SW30) and (b, d) GO-functionalized (SW30-GO) polyamide membrane surfaces.

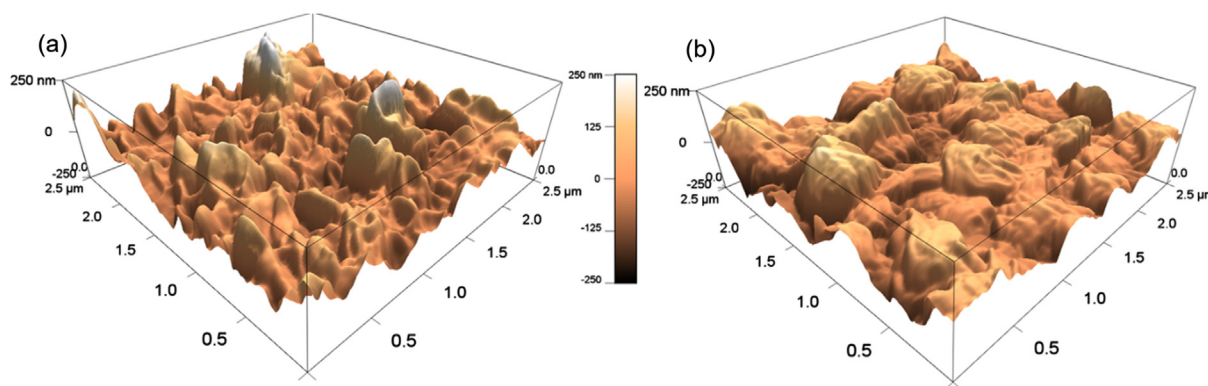


Fig. 3. Tapping mode AFM images of (a) control (SW30) and (b) GO-functionalized (SW30-GO) polyamide membrane surfaces.

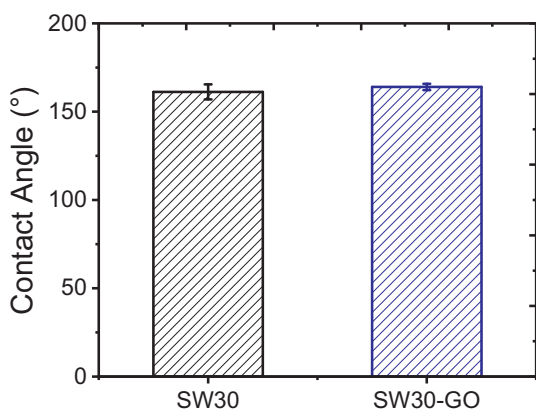


Fig. 4. Contact angles obtained through the captive bubble method using *n*-decane droplets in ultrapure water. The average of 12 *n*-decane droplets recorded over two membrane specimens of each type is shown. Error bars denote one standard deviation.

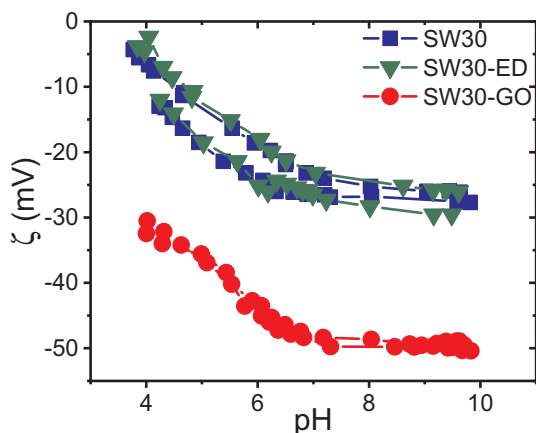


Fig. 5. ζ -potential of control (SW30), ethylenediamine-modified (SW30-ED), and GO-functionalized (SW30-GO) polyamide membranes over the pH range 4–10. Measurements were performed in a 1 mM KCl background electrolyte. Results are shown for two samples of each membrane type.

control and ED-functionalized surfaces. We attribute the increase in negative charge of the membrane surface to a higher surface density of carboxylate functional groups derived from the GO nanosheets [40,41]. A similar increase in the negative charge of polyamide membranes after GO modification has been reported by others [42,43]. These results provide further confirmation of the successful functionalization of the membrane surfaces with GO.

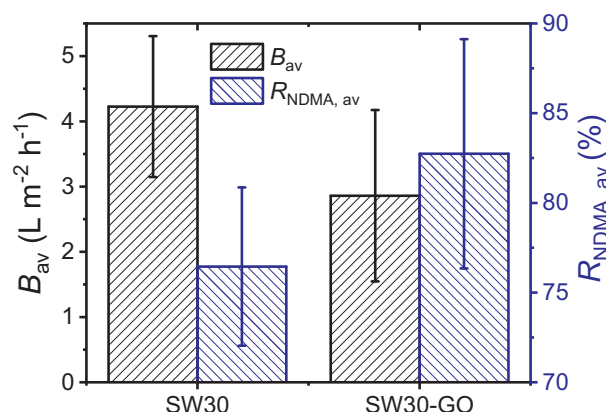


Fig. 6. Average NDMA permeability coefficient (B_{av}) and average NDMA rejection coefficient ($R_{NDMA, av}$) of control (SW30) and GO-functionalized (SW30-GO) polyamide membranes. The results shown are averages of six SW30 and seven SW30-GO membrane coupons. Error bars indicate one standard deviation.

3.2. Effect of GO surface functionalization on NDMA rejection

Figs. 6 and 7 present the average water permeability coefficient (A_{av}), average NDMA permeability coefficient (B_{av}), and average NDMA rejection coefficient ($R_{NDMA, av}$), obtained from six SW30 filtration experiments and seven filtration experiments with independently functionalized SW30-GO membrane samples. In addition, Fig. 7 presents the average water/NDMA permselectivity, $(A/B)_{av}$.

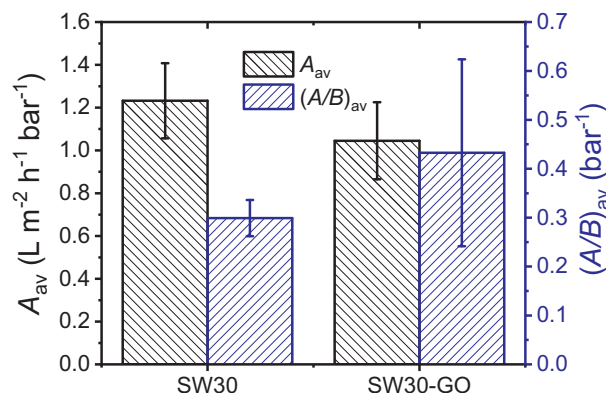


Fig. 7. Average water permeability coefficient (A_{av}) and average water/NDMA permselectivity $(A/B)_{av}$ of control (SW30) and GO-functionalized (SW30-GO) polyamide membranes. The results shown are averages of six SW30 and seven SW30-GO membrane coupons. Error bars indicate one standard deviation.

Fig. 6 demonstrates that GO surface modification improves NDMA rejection ($R_{\text{NDMA, av}}$) by 6.2%, increasing from 76.5% for SW30 to 82.7% for SW30-GO ($p = 0.068$). The improved removal of NDMA is similarly manifested by a decrease in B_{av} from $4.2 \text{ L m}^{-2} \text{ h}^{-1}$ (LMH) for SW30 to 2.9 LMH for SW30-GO ($p = 0.068$). We further investigated the role of the ED linker in NDMA removal: the NDMA rejection coefficient of SW30-ED, 80.2%, showed that ethylenediamine plays a role in NDMA rejection, though additional gains in nitrosamine removal are due to the combined ED-GO surface modification. SW30-GO membranes will thus be the focus of the discussion that follows.

Fig. 7 shows that improved rejection is observed at the expense of a 13% decrease in water permeability, with A_{av} decreasing from 1.2 LMH bar^{-1} for SW30 (a value consistent with that specified by the manufacturer, *i.e.*, 1.1 LMH bar^{-1}) to $1.05 \text{ LMH bar}^{-1}$ (SW30-GO) ($p = 0.086$). The observed decrease in water permeability is due to the additional hydraulic resistance derived from the GO layer, and reflects the well-known tradeoff between water permeability and membrane separation performance [2,15,44]. We note that the decrease in A_{av} is smaller than that observed following heat treatment (20–35%) [15], a strategy pursued by others to achieve high (92%) nitrosamine removal, albeit with significant loss of water permeance [15]. Moreover, improved NDMA rejection observed with GO functionalization results in improved water/NDMA permselectivity, $(A/B)_{\text{av}}$, which increases from 0.3 bar^{-1} to 0.43 bar^{-1} ($p = 0.12$) following GO surface modification, as shown in Fig. 7.

Figs. 8 and 9 present the results of the individual filtration experiments from which the average quantities in Figs. 6 and 7 were computed. We observe significant variability in membrane transport properties across SW30 and SW30-GO coupons, which is nonetheless within the expected range specified by the manufacturer ($\pm 15\%$ [45]). Variation in transport properties across specimens of the same membrane type is a common feature of polyamide membrane materials [20,46]. For control membranes, the variability in transport properties and selectivity is likely due to regions in SW30HR polyamide that possess different chemical compositions. As observed by others [21], SW30HR polyamide exhibits nitrogen-rich regions (comprising $\sim 8\text{--}10\%$ N and $\leq 20\%$ O), and nitrogen-poor regions ($1\text{--}3\%$ N and $24\text{--}33\%$ O) indicative of a proprietary surface coating that does not uniformly cover polyamide [21,47–50].

For the six control (SW30) coupons investigated, A varies from 1 LMH bar^{-1} to 1.4 LMH bar^{-1} . Within this range, NDMA rejection decreases from 81% to 72% (Fig. 8); similarly, the NDMA permeability coefficient (B) is shown to increase from 3.1 LMH to 5.3 LMH as A

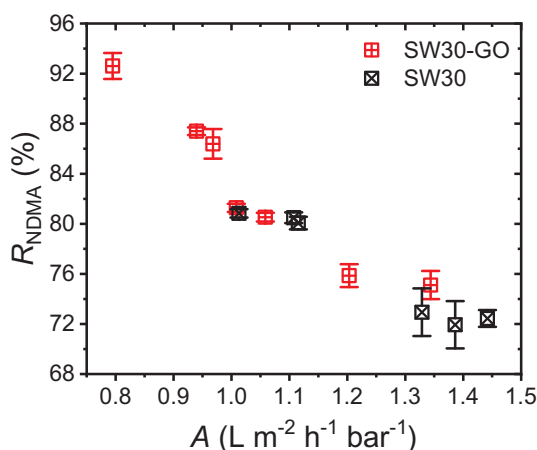


Fig. 8. Dependence of NDMA rejection coefficient (R_{NDMA}) on water permeability coefficient (A) for individual membrane filtration experiments with control (SW30) and GO-functionalized (SW30-GO) membrane specimens. R_{NDMA} denotes the mean rejection based on three feed and permeate samples (error bars indicate one standard deviation).

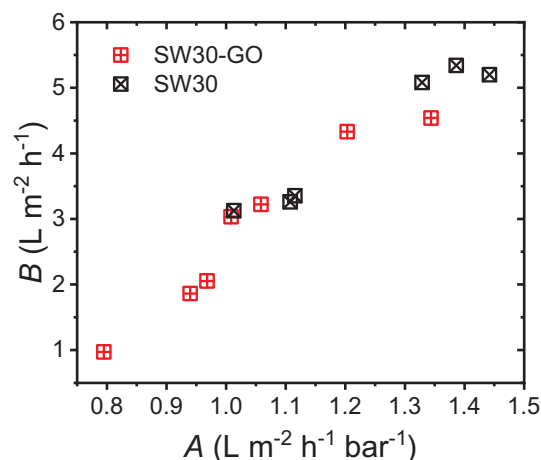


Fig. 9. Dependence of NDMA permeability coefficient (B) on water permeability coefficient (A) for individual membrane filtration experiments with control (SW30) and GO-functionalized (SW30-GO) membrane specimens.

increases (Fig. 9), *i.e.*, the observed dependence of R_{NDMA} and B on A is consistent with the permeability-selectivity tradeoff. Similar variability is observed across individual GO-modified membrane specimens; this variation can be attributed to the chemically distinct regions of the underlying polyamide layer, and is possibly compounded by a somewhat heterogeneous GO coating (observe the GO-lean regions in the Raman maps shown in Fig. 1). Accordingly, NDMA removal is observed to decrease from 93% to 75% (equivalent to an increase in B from 1.0 LMH to 4.5 LMH) as the water permeability coefficient increases from 0.8 to 1.3 LMH bar^{-1} .

Contaminant removal by reverse osmosis is derived from multiple physical and chemical properties of the membranes: surface chemistry (*i.e.*, hydrophobicity or hydrophilicity) affects contaminant partitioning into the membrane [7,21,51]; further, membrane surface charge strongly influences rejection of charged species through Donnan exclusion [52]; finally, nanoscale voids in polyamide modulate water and contaminant transport across the polymer film [4,9]. Membrane hydrophobicity and charge do not explain the increase of NDMA rejection observed above with SW30-GO membranes, given that NDMA is uncharged at circumneutral pH [15], rendering Donnan exclusion inoperable. Moreover, SW30 and SW30-GO specimens showed similar wetting by *n*-decane (Fig. 4), suggesting that the GO coating does not noticeably affect hydrophilicity and NDMA partitioning. On the other hand, the observation that the highest NDMA rejection is exhibited by membrane specimens with relatively low A (Fig. 8) suggests that the improved NDMA removal observed in GO-functionalized membranes may be due to obstruction of nanoscale defects in polyamide by the ED-mediated tethering of GO nanosheets. Defects in polyamide, present as free-volume cavities $\sim 0.27 \text{ nm}$ in radius [4], are blocked by the covalently bonded layer of GO nanosheets, which are themselves impermeable to water and solutes [53,54], leading to improved removal of NDMA by steric exclusion.

4. Concluding remarks

Development of membranes demonstrating high rejection of SNSs remains a long-standing challenge in membrane separations. Focusing on NDMA, a carcinogenic SNS of significant concern in wastewater reclamation, we have shown that surface functionalization of commercial polyamide membranes with GO nanosheets – a building block of membrane biocidal coatings – results in improved NDMA rejection. We draw the following conclusions from our study:

- Compared to control membranes, GO-functionalized (SW30-GO)

membranes improve NDMA rejection by 6.2%, increasing from 76.5% to 82.7%. We ascribe the improvement in NDMA removal to sealing of defects in polyamide by the covalently bonded GO layer.

- The improved NDMA rejection occurs at the expense of a 13% decrease in water permeability coefficient, due to the higher hydraulic resistance caused by the GO layer. Nevertheless, the loss of water permeance appears to be moderate, given that an increase in the water/NDMA permselectivity from 0.3 bar⁻¹ to 0.43 bar⁻¹ is also observed.
- In contrast with other surface modification strategies, membrane functionalization with GO does not negatively alter the interfacial properties of the polyamide (notably hydrophobicity and roughness), making this a promising strategy for the modification of membranes for wastewater reclamation.

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Graphene Oxide Surface Modification of Polyamide Reverse Osmosis Membranes for Improved *N*-Nitrosodimethylamine (NDMA) Removal

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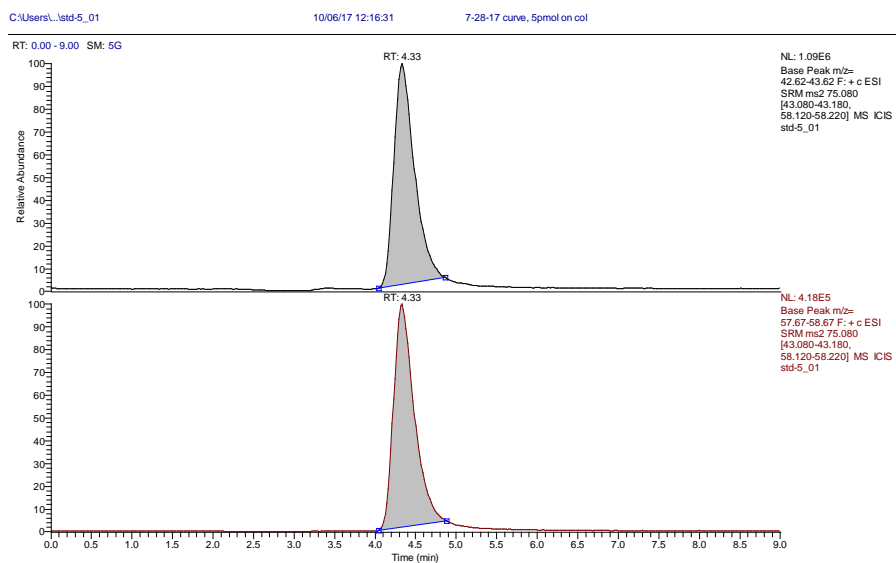


Figure S1. Chromatogram of a synthetic standard mixture (5 pmol injected into column). The top image corresponds to the quantitative channel, while the bottom image is that of the qualifier ion.